

# ELECTROLYTE BASED ON-DEMAND AND DISPOSABLE MICROBATTERY

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## ABSTRACT

A micromachined battery based on liquid electrolyte and metal electrodes for on-demand and disposable usages has been successfully demonstrated. The microbattery with gold as the positive electrode and zinc as the negative electrode is fabricated by using the surface micromachining technology and tested with electrolyte consisting of sulfuric acid and hydrogen peroxide. The operation of the battery can be on-demand by putting a droplet of electrolyte to activate the operation. Theoretical voltage and capacity of the microbattery are formulated and compared with experimental results. The experimental study shows that a maximum voltage of 1.5V and maximum capacity of 122.2 $\mu$ W-min have been achieved.

## INTRODUCTION

Micro power generation aims at generating power at the micro scale has been an important topic. Various approaches to supply power for micro scale devices are now being investigated to enable standalone micro sensors, actuators and future nano-structures for various types of functionalities. The advantages of these MEMS systems are severely limited by the associated bulk batteries and the capability of providing power source may well be the bottleneck for future nano-structures. Some of the initial demonstrations on micro fuel cells research have shown very promising results toward the concept of "macro power from micro machinery" [1]. Most of these projects use hydrogen, oxygen and other fuels to generate micro combustion and target 10 to 100Watts of continuous power supply [2]. However, in order to fabricate the combustion chambers or fuel cells for these micro power sources, it generally requires complicated micromachining processes. For example, MIT's micro turbine project needs a 5-wafer bonding process that is not compatible with most of the other MEMS processes [3]. Furthermore, the manufacturing cost for these micropower sources appears to be high and may not be competitive economically.

On the other hand, microbattery with low cost and high capacity is desirable for MEMS devices [4-6]. Previously, solar cell [7] and rechargeable microbattery [8] have been investigated by using rather complicated micromachining processes. Microbattery that offers good capacity, suitable service time and compatible manufacturing process with active devices will have plenty of applications for MEMS devices. For example, disposal

microsystems such as diagnostic devices, DNA chips, and even disposal microtransceivers will be best equipped with an on-demand, and disposal microbattery.

## MICROBATTERY THEORY

Figure 1 illustrates the schematic of the electrolyte based, on-demand and disposable microbattery which consists of a positive electrode (gold), a negative electrode (zinc), and an electrolyte cavity. A pair of supports is used to form the cavity between the positive and negative electrodes. The operation of the microbattery can be on-demand by putting a droplet of electrolyte in front of the cavity as shown Fig. 2. Surface tension force drives the electrolyte into and fill up the cavity. When the battery is connected to an external load, the electro-chemical reaction occurs. Electrons, generated at the negative electrode (zinc), flow through the load resistor as shown in Fig. 1 and are collected at the positive electrode (gold). In this preliminary demonstration, sulfuric acid ( $H_2SO_4$ ) is chosen as the liquid electrolyte, gold is used as the positive electrode and zinc is used as the negative electrode. Hydrogen peroxide ( $H_2O_2$ ) is added to remove hydrogen gas in the microbattery. It is noted that gold is the electron collector and is not reactive in the process.

The electro-chemical reactions of the microbattery at the zinc electrode can be expressed as the anodic reaction (oxidation):

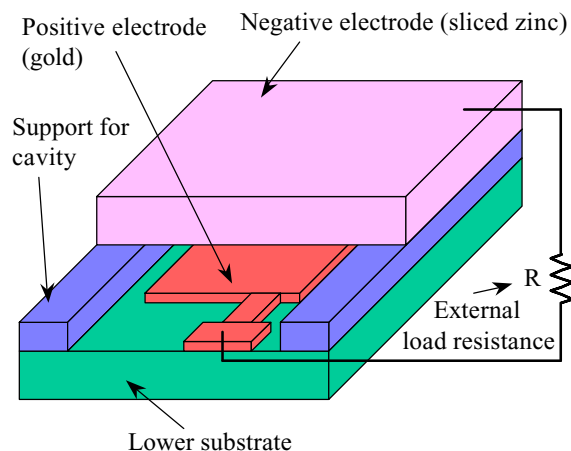
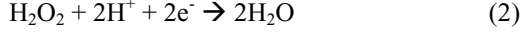


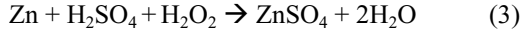
Fig.1. Schematic of a electrolyte on-demand and disposal microbattery: both positive electrode (gold) and supports for forming the electrolyte cavity are placed on the lower substrate while the negative electrode (zinc) is capped; the microbattery works after putting liquid electrolyte (see Fig. 2).



the cathodic reaction (reduction) is represented as:



and the overall reaction is:



It is observed from Eqs.(1)-(3) that the electrons flow through the external load resistor and ions of  $\text{H}^+$  and  $\text{SO}_4^{2-}$  flow within the electrolyte, inside the cavity. The theoretical voltage can be obtained from the change in the Gibbs free function between reactants and products as follows [9]:

$$V^\circ = \frac{-\Delta G^\circ}{nF} \quad (4)$$

where  $V^\circ$ ,  $\Delta G^\circ$ ,  $n$  and  $F$  denote the standard voltage, the Gibbs free energy at the standard state, the number of moles of the changed electrons during the reaction, and Faraday defined by 96500 Coulombs, respectively. The Gibbs free energy change of the reaction in Eq.(4) can be written as [10]:

$$\Delta G^\circ = \Sigma(\Delta G^\circ)_p - \Sigma(\Delta G^\circ)_r \quad (5)$$

where subscripts  $p$  and  $r$  indicate products and reactants in Eq.(3), respectively. Using Eqs.(4)-(5) and the Gibbs free energy in Table 1, the standard voltage,  $V^\circ$ , in the case of tested microbattery is calculated as  $V^\circ = -(-483850)/(2 \times 96500) = 2.5\text{V}$ .

Table 1. Gibbs free energies and weights of the chemicals

	Chemical	$\Delta G^\circ$ [kJ/mol]	Weight [g/mol]
Reactants	Zn	0 (definition)	65.37
	$\text{H}_2\text{SO}_4$	-744.53	98.08
	$\text{H}_2\text{O}_2$	-120.35	34.02
Products	$\text{ZnSO}_4$	-891.59	161.43
	$\text{H}_2\text{O}$	-228.57	18.02

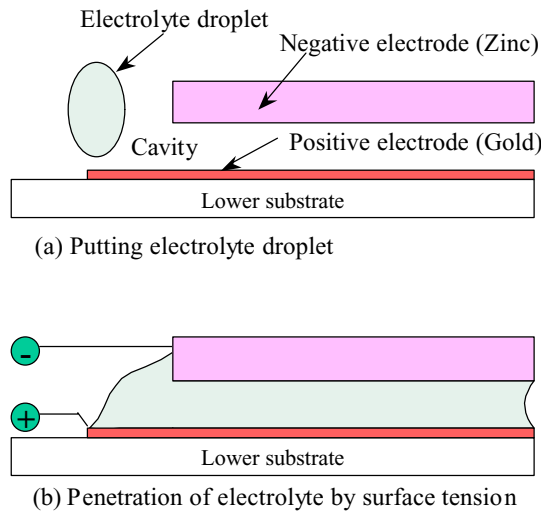


Fig.2. Working principle of the microbattery: (a) upon putting a liquid-electrolyte droplet in front of the cavity, the electrolyte penetrates into the cavity by surface tension; (b) the microbattery works to supply power.

In order to obtain the theoretical capacity of the microbattery, electrons per mole of the reactants are used. From Eqs.(1) and (2), two moles of electrons move from the anode (Zn) to the cathode ( $\text{H}_2\text{O}_2$ ) through the external load resistor when one mole of each reactant consumes as shown in Eq.(3). Therefore the theoretical electron capacity,  $C_{el}$ , can be expressed as follows:

$$C_{el} = \frac{nF}{\Sigma \text{ weight of reactant}} \quad (6)$$

The theoretical capacity,  $C_{el}$ , is calculated from Eq.(6) and the data of Table 1 as  $C_{el} = 2 \times 96500 / (65.37 + 98.08 + 34.02) = 977.17\text{C/g} = 0.271\text{Ah/g} = 16.3\text{Amin/g}$ . Energy capacity,  $C_{en}$ , is obtained as  $C_{en} = V^\circ C_{el} = 2.5 \times 0.271 = 0.678\text{Wh/g} = 40.7\text{Wmin/g}$ . Therefore, the theoretical voltage and capacity of this microbattery using zinc, sulfuric acid and hydrogen peroxide are 2.5V and 0.271Ah/g that are comparable to those of 2.8V and 0.271Ah/g of the magnesium battery [9].

## FABRICATION

The disposable microbattery has been designed and fabricated by a surface micromachining process [11]. The process starts with the growth of a  $0.6\mu\text{m}$ -thick low stress LPCVD (Low Pressure Chemical Vapor Deposition) silicon nitride layer on the silicon substrate as an electric isolation layer. In the processing step of Fig. 3(a), a  $0.5\mu\text{m}$ -thick LPCVD polysilicon (poly0) is deposited and patterned for the basis of the electrolyte cavity support. A  $2\mu\text{m}$ -thick sacrificial PSG (phosphosilicate glass) layer is deposited in the step of Fig. 3(b). Figure 3(c) shows that a  $2\mu\text{m}$ -thick polysilicon (poly1) is deposited and patterned for constructing the support. Afterwards, a  $0.75\mu\text{m}$ -thick PSG2 layer is deposited and patterned as shown in Fig. 3(d). A LPCVD  $1.5\mu\text{m}$ -thick polysilicon (poly2) is deposited and patterned for the positive electrode and the support in Fig. 3(e). A  $0.5\mu\text{m}$ -thick gold layer for

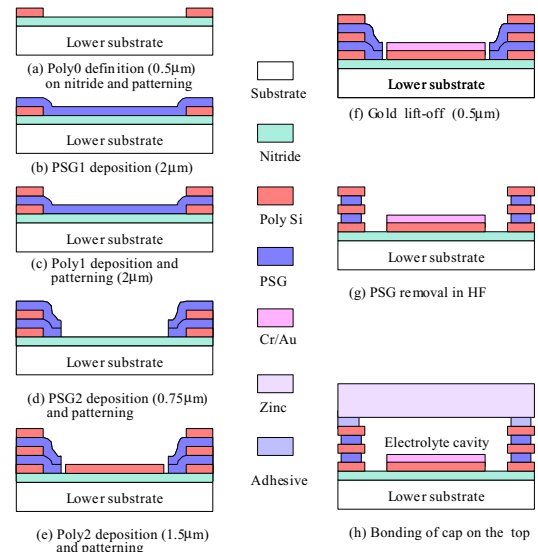


Fig.3. Fabrication process for the microbattery.

positive electrode and contact pads is then deposited and patterned using lift-off in the processing step of Fig. 3(f). After the removal (Fig. 3(g)) of the sacrificial PSG layers using HF solution to construct the electrolyte cavity, the microbattery wafer is rinsed and dried. The process is completed by bonding a sliced piece of zinc on the top of lower substrate [12] of microbattery as shown in Fig. 3(h). Figure 4 shows a SEM photograph of the fabricated microbattery up to the process step of Fig. 3(g) before capping with and the chip size is 1mm x 1mm. Gold electrode with an area of  $600\mu\text{m} \times 850\mu\text{m}$  and two cavity supports are constructed as shown. Figure 5 is a close view of area C in Fig. 4 showing a contact pad, part of cavity support and part of gold layer used for the positive electrode. Figure 6 shows the SEM photograph of capped microbattery before putting a droplet of the electrolyte. The cap substrate, cavity and wires for experimental measurement are also shown.

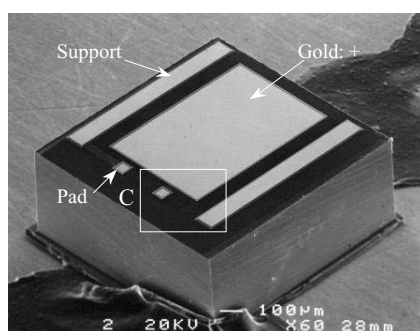


Fig.4. SEM photograph of a fabricated microbattery before capping; the size is 1mm x 1mm.

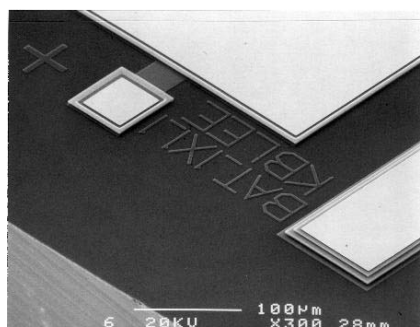


Fig.5. Close view of C in Fig. 4 showing the positive electrode (gold), a pad and the capacity support.

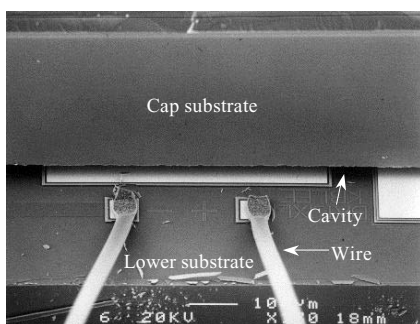


Fig.6. SEM photograph of capped microbattery before putting the electrolyte.

## RESULTS AND DISCUSSIONS

The output voltage of the microbattery has been measured with respect to time for various combinations of electrolyte concentration and load resistors. After placing a droplet of  $0.5\mu\text{l}$  in front of the cavity (Fig. 2), voltage has been measured by a voltmeter. The molarity of the hydrogen peroxide is set at 10% higher than that of the sulfuric acid in order to eliminate the generated hydrogen gas in all experiments.

Figures 7-10 show the measured voltages of the microbattery when changing the concentration of sulfuric acid and the load resistance. It is noted from Figs. 7-9 that higher concentration of sulfuric acid results in higher voltage output, and higher load resistance results in longer service time but smaller output current. In Fig. 10, the service period of the 2.0M sulfuric acid is shorter than that of the 1.5M sulfuric acid in Fig. 9 due to the generation of hydrogen bubbles in the electrolyte. It is observed from Fig. 9 that the measured maximum voltage of this microbattery is 1.5V in the case of 1.5M sulfuric acid with a load resistance of  $1\text{M}\Omega$ . Although the measured voltage of 1.5V is less than the theoretical voltage of 2.5V, obtained from Eqs. (4) and (5), it is sufficient to drive low voltage microelectronics. The service time of this prototype microbattery that has voltage output over 1.0V is approximately 10 minutes in Figs. 8 and 9 when using the resistance of  $1\text{M}\Omega$  and sulfuric acid molarity of 1M and 1.5M.

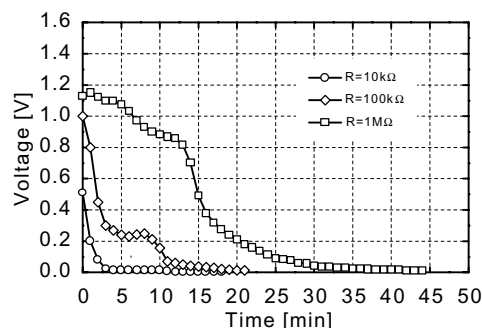


Fig.7. Measured voltage of the microbattery with 0.5M sulfuric acid.

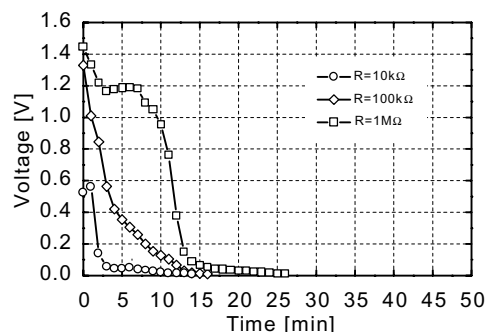


Fig.8. Measured voltage of the microbattery with 1.0M sulfuric acid

Table 2 compares energy capacity obtained from numerical integration of data from Figs. 7-10. Energy capacity,  $C_{en}$ , of the microbattery is calculated as follows:

$$C_{en} = \int \frac{V^2}{R} dt \quad (7)$$

where  $V$ ,  $R$  and  $t$  denote the measured voltage, the load resistance and time, respectively. It is noted from Table 2 that energy capacity of the microbattery decreases with the load resistance, and increases with the concentration of the sulfuric acid. There are cases in 2M sulfuric acid electrolyte tests that hydrogen bubbles are generated and the energy capacity decreases as compared with the 1.5M sulfuric acid electrolyte. The combination of 2.0M sulfuric acid and 10k $\Omega$  offers maximum energy capacity of 122.2  $\mu$ W-min.

Table 2. Energy capacities obtained from Figs. 7-10

	10k $\Omega$	100k $\Omega$	1M $\Omega$
0.5M	17.9	18.2	14.7
1M	48.4	34.9	15.2
1.5M	117.7	82.0	21.6
2M	122.2	68.0	4.38

Energy capacity in  $\mu$ W-min

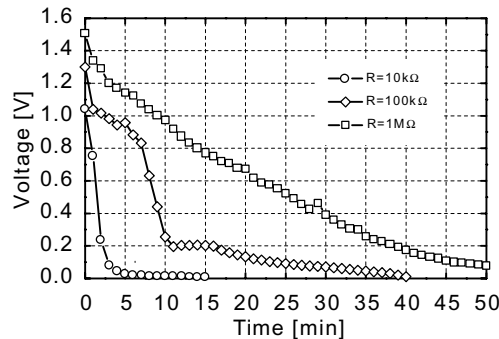


Fig.9. Measured voltage of the microbattery with 1.5M sulfuric acid.

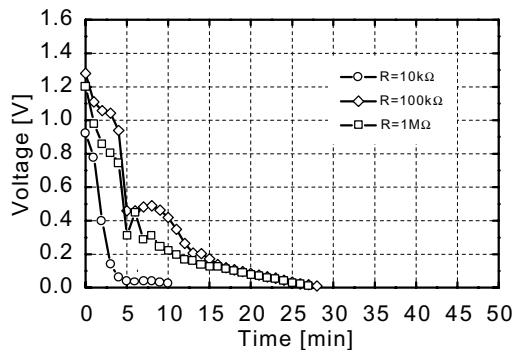


Fig.10. Measured voltage of the microbattery with 2.0M sulfuric acid. Bubble generation is observed.

## CONCLUSIONS

We have successfully demonstrated a micromachined battery based on liquid electrolyte and metal electrodes for on-demand and disposal usages. Basic concept of a disposal microbattery is presented and the prototype microbattery is fabricated by using the surface micromachining technology. In this preliminary demonstration, sulfuric acid is chosen as the electrolyte and hydrogen peroxide is used to remove hydrogen gas. Gold is chosen as the positive electrode for collecting electrons and zinc is used as the negative electrode for offering electrons. The experimental study on the microbattery demonstrated that a maximum voltage of 1.5V, energy of capacity of 122.2 $\mu$ W-min has been achieved. It is foreseeable that the voltage, current and capacity of the microbattery can be improved by making series, parallel battery designs as well as by choosing other electrolyte system. This battery can be used for on-demand and disposable MEMS devices that urgently require low cost, small size power sources that are compatible with common MEMS fabrication process, including the CMOS process.

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